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## REMARKS

### **Amendment To The Specification**

This supplemental response is in response to the interview between Examiner CHEVALIER and Applicants' Canadian and US agents of record, Lynn C. Schumacher and Ralph Dowell, respectively. Applicants and the two agents of record would like to thank the Examiner for taking the time to meet with them on July 9, 2004. At this interview Applicants' agents pointed out to the Examiner an Abstract by Professor Younan Xia in which Applicants' work was described in one aspect as overcoming problems with the prior art. The citation, Yadong Yin and Younan Xia, "**Growth Of Large Colloidal Crystals With Their (100) Planes Oriented Parallel To The Surfaces Of Supporting Substrates**", Advanced Materials, 2002, 14, No. 8, April 18, pages 605-608; is being provided herewith and discussed hereinafter.

In addition, another publication by experts in the field which refers to publications by the Applicants related to the present application is being submitted herewith, Jau-Ya et al. "**Actively Controlled Self-Assembly of Colloidal Crystals in Microfluidic Networks by Electrocapillary Forces**", J.

Am. Chem. Society, 2004, 126, 8096-8097, is being provided herewith and discussed hereinafter.

Neither of the above articles are prior art and are submitted to show recognized differences between the present invention and the cited prior art.

Claims 87, 88, 89 and 91 have been amended to more clearly recite the product being produced in the product by process claim.

### **Patentability of the Claims Over the Cited References**

As discussed with the Examiner at the interview, the publication, Yadong Yin and Yournan Xia, "**Growth Of Large Colloidal Crystals With Their (100) Planes Oriented Parallel To The Surfaces Of Supporting Substrates**", Advanced Materials, 2002, 14, No. 8, April 18, pages 605-608, makes clear mention of Applicants publication related to the present invention and how it solves problems in the prior art. This is mentioned on page 606, lines 14 to 20, and reference is made to the Ozin et al. paper in reference 15, dated before Applicants' provisional filing date.

In addition, the publication Jau-Ya et al. "**Actively Controlled Self-Assembly of Colloidal Crystals in Microfluidic Networks by Electrocapillary**

**Forces", J. Am. Chem. Society, 2004, 126, 8096-8097 discloses in general terms the usefulness of Applicants' invention for production of optical components using colloidal crystals assembled with other planar optical components, see the highlighted section on page 8091.**

Claims 1-14 and 87-90 have been rejected under 35 U.S.C. § 102(b) as being anticipated by the reference United States Patent No. 6,436,187 B1 ('187) issued to Patel et al. Reconsideration of the grounds for rejection under 35 U.S.C. § 102(b) is respectfully solicited for the following reasons.

Patel et al. is directed to a method of producing a colloidal crystal template onto which colloidal crystals are grown. This is achieved by using a surface relief pattern, which satisfies several conditions. Patel notes that the problem they are trying to solve relates to templates such as those provided by Blaaderen (column 2, lines 42-44 which have a "*cross-sectional structure having 90° angles between the hole walls 12 and the template surface 14.*" as shown in Figure 1 of Patel.

This is also discussed in column 4, lines 27 to 38 of Patel. Due to electric field distortions near the corners this prevents the colloidal particles settling into the channels-also shown in Figure 1 of Patel. Patel discloses overcoming this problem by making a template as shown in Figure 2 of Patel. The Examiner's

attention is directed to column 3, lines 1 to 8 where Patel discusses their template is produced with rounded edges and alternative methods for producing their templates are discussed in column 6, lines 1 to 13.

The disclosure referred to by the Examiner in column 3, lines 9 to 36 simply defines Patel's definition of a colloidal template made by their method (lines 9-24) and gives Patel's guidelines for producing the template (lines 25-36). These guidelines are further expounded on in column 5, lines 6 to 46. Once the template has been produced typically having dimensions on the order of a sphere to be deposited therein (Figures 2 and 3 of Patel), a first layer of colloidal particles is deposited into the template, after which the 3D colloidal crystal is grown on top of the this first layer. Therefore, Patel describes a method to create three-dimensional colloidal crystals by using a surface relief pattern, which acts as a guide for the first layer of colloidal spheres deposited onto it. Once this first layer is deposited in a **square arrangement** (see Fig. 4 of Patel) and claim 1, line 48) subsequent deposition of new sphere layers would supposedly give rise to the three dimensional structure that is claimed in their patent.

In the first instance, while Patel et al. order a **single layer** of spheres onto a surface relief pattern, the present invention by contrast orders a **whole** colloidal

crystal **within** the surface relief patterns. However, as discussed with the Examiner, the present invention, as embodied in claim 1, allows one to build colloidal lattices **within** surface relief patterns that will host **the whole structure**. While Patel et al. invention only describes how to template the crystallization of a **single** square or hexagonally arranged sphere layer **onto** a large area surface presenting a surface relief pattern in which the depth of the relief is always of the order of a single sphere diameter or less.

Secondly, Patel discloses the need for the template structure to have a periodicity, see for example the first *principle* (column 5, line 10) of making the template as disclosed in column 5, lines 14 to 23. Applicants surface features are not in any way restricted since the closed wells or indentations or open or closed channels are not required to be periodic across the surface, which is a reflection of the point made above that photonic crystals may be grown in each of the surface features. In addition, while Patel requires rounded edges of his template, (column 6, lines 5 to 10), Applicants surface relief pattern does not require this.

In addition, Patel is silent with respect to obtaining photonic crystals as have been achieved with Applicants products embodied by claim 1. Thus, on several points Patel teaches away from the present invention, and Applicants

respectfully submit Patel does not disclose the subject matter of present claims 1-14 and 87-90.

Claims 1-6 and 87-90 have been rejected under 35 U.S.C. § 102(b) as being anticipated by the reference to Gates et al. in their publication: **“Self/assembly of meso and nanoparticles into 3D ordered arrays and its applications”**, Proceedings of the Materials Research Society, Spring Meeting 1999, pages 149-154. Reconsideration of the grounds for rejection under 35 U.S.C. § 102(b) is respectfully solicited for the following reasons.

Gates teaches how to create three-dimensional arrays of colloidal particles whereby, as disclosed on page 149, lines 25 to 27: *“colloidal particles are self-assembled into cubic close packed (ccp) arrays under the confinement of a specially designed cell”*. This specially designed “packing cell” (line 2, page 150) of Gates is two glass plates, with a square frame of photoresist sandwiched between them and held together by binder clips. Gates et al. teach in their paper that these two parallel glass plates are separated by this thin photoresist frame through which channels have been drilled to allow the liquid in which the colloid particles are suspended to flow out of the space confined between the two parallel plates. Therefore, these channels are just the drainpipes for removing the

solvent from the sphere suspension inserted between the plates and no crystallization takes place therein. In other words, the colloidal particles are confined within two glass parallel plates, but none of them possess a surface relief pattern as recited in claim 1 of the present application.

Further, as seen on page 151, lines 8 to 10 and figure 1B, the two glass substrates are removed to give a free standing structure formed of a cubic close packed array. Thus, to emphasize this point, the channels in Gates et al. have nothing to do with surface relief patterns as described and used in Applicants' claim 1, they are completely different and used for an entirely different purpose, just drainage for the solvent in which spheres are suspended not crystallization of spheres.

Finally, the present invention as recited in claim 1 provides colloidal photonic crystals formed in each of the surface features which exhibit Bragg diffraction. There is no teaching of this in Gates.

Claims 1-4, 15, 16 and 87-90 have been rejected under 35 U.S.C. § 102(b) as being anticipated by the reference to Clark et al. (U.S. Patent No. 4,728,591). Reconsideration of the grounds for rejection under 35 U.S.C. § 102(b) is respectfully solicited for the following reasons.

The Examiner has taken the position that based on Clark's disclosure in column 3, lines 24 – 31 and column 5, lines 33-54 that this reference teaches producing a surface relief pattern in the substrate surface and self-assembling colloidal particles in such pattern. The thrust of Clark's invention is to provide articles having nanometer scale features on a surface of the article. Referring to the Abstract, Clark states these are produced by "*employing a substrate base or coating and a thin layer serving as a lithographic mask or template, consisting of a self-assembled ordered material array, typically a periodic array of molecules* ...". Later, in column 2, line 30 and 31 it is specified "Such nanostructures are based on nanometer patterns created by self-assembled two-dimensional arrays".

In contrast, the present invention as recited in claim 1 provides colloidal photonic crystals formed in each of the surface features, which exhibit Bragg diffraction. Clark is completely silent with respect to this type of composite material and provides no disclosure whatsoever that would lead anyone skilled in the art to the subject matter of claim 1.

Claims 91-94 have been rejected under 35 U.S.C. § 102(b) as being anticipated by the reference to Asher et al. (U.S. patent No. 6,014,246).

Reconsideration of the grounds for rejection under 35 U.S.C. § 102(b) is

respectfully solicited for the following reasons.

Claims 91 and 92 have been amended to more clearly define the product produced by the methods recited in each of these claims. Applicants' review of Asher shows the latter teaches a colloidal array maintained in an aqueous medium, see column 4, lines 48-54, note lines 50 to 52 in particular, and independent claims 1 and 11, 18, 28 (hydrogel). In one embodiment shown in Figure 2 of Asher the array is maintained in a chamber 16 containing water 14 and particles 12 forming a dispersion in the water, see column 6, lines 66 to column 7, line 5 where the ratio of water to particles is disclosed as being a variable so as to effect the diffraction wavelength. In another embodiment of the array Asher discloses using a hydrogel to contain the colloidal particles as disclosed in column 8, lines 12 to 44 of Asher.

Claim 92 of the present application recites a lattice parameter modulated colloidal crystal film based on regions containing differently sized particles built on top of a planar substrate and has been rejected by the Examiner on the basis of the previous disclosure of a similar product by Asher et al. in the aforementioned patent. In the sections of Asher's patent referred to by the

examiner (col. 9, lines 1-62; col. 5, lines 41-56), what is pointed out is the fact that their materials can be made of spheres of different diameter which would lead to different diffraction peaks. However, Asher does not teach two different sized particle types would coexist in the same film forming alternating particle size colloidal crystals and leading to a periodic variation of the optical properties, as it happens in the structure of claim 92. In fact, the production methods disclosed by Asher do not allow such a product to be obtained. Mixture of spheres of a different type, composition or size, in Asher's preparation substance can only lead to a different crystalline structure of the whole lattice (called a binary colloidal crystal) or disorder, but not to periodically alternated colloidal crystal microchannels having particles of different sizes contained in each.

Thus, Applicants respectfully submit the subject matter of claims 91 and 92 are not disclosed in Asher, and certainly the products formed by Asher are not formed according to the method of formation recited in claims 91 and 92. In view of this Applicants submit claims 91 to 94 are patentably distinguishable over Asher.

The examiner has rejected claims 96-97 under 35 U.S.C. § 102(b) as being anticipated by on the basis of being anticipated by Maenosomo et al. (U.S.

Patent No. 6,337,117). In the Maenosomo patent, their colloidal particles are luminescent nanoparticles, which luminesce, that is, they present luminescence (col. 11, lines 3-11; col. 12, lines 43-61). Further, “the particle size distribution of nanoparticles is arbitrary” (col. 14, lines 4 and 5), since the optical effects they make use of are not based on diffraction, as in the present application, which would require a narrow particle size distribution and the precise ordering of the particles in a particular lattice. This is why in claim 96 there is recited a “first array of first colloidal particles of a **first size**... and a second array of second colloidal particles of a **second size**”, which in the case of spherical particles these will be monodisperse. Further, their product is based on particles whose size ranges between 0.05 nm and 100 nm (col. 11, line 5). Particle sizes must be limited to this range and display so-called quantum size effects (scale tunable electronic properties) for their invention to work, as they point out explicitly (col. 11, lines 6-8), a limitation not applicable to the present invention. Furthermore, their product displays different colors in different regions of the film as a result of the different luminescence of the particles in each region of the film (col. 14, lines 23-30), which results from the different particle size or composition in each one of these regions. In our case, in contradistinction the different colors displayed by the

different parts of the film result from the different diffraction taking place in the different sphere size colloidal crystals that form it. In their case, electronic excitation of the particles is needed in order to cause the emission of light from them and observe different colors. In the present invention, as recited in the claims, what is observed is Bragg diffraction so that simple illumination under white light is enough to see different colors.

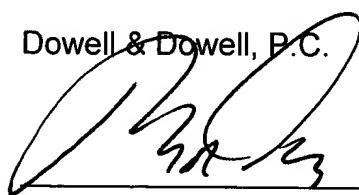
In view of the foregoing, reconsideration and withdrawal of the rejection of claims 14-33 is respectfully solicited and favorable consideration and allowance of claims 14-33 and 66 is requested.

As a result of the interview, the amendments previously submitted with respect to claim 1 have now been made to claims 87, 88, and 89. Further, all withdrawn claims have been cancelled without prejudice subject to applicants' right to file divisional applications with respect thereto.

Should the Examiner have any questions regarding the allowability of the claims with respect to the art, it would be appreciated if the Examiner would contact the undersigned attorney-of-record at the telephone number shown below for further expediting the prosecution of the application.

Respectfully submitted,

Dowell & Dowell, P.C.

A handwritten signature in black ink, appearing to read "Ralph A. Dowell".

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## Actively Controlled Self-Assembly of Colloidal Crystals in Microfluidic Networks by Electrocillary Forces

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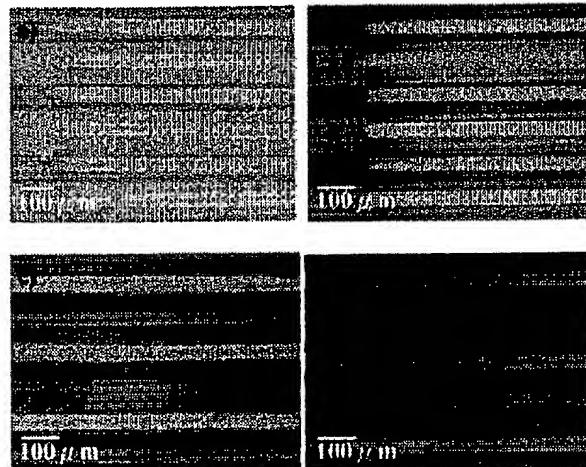
Self-assembly is a commonly used strategy in synthesis and fabrication. One of the most economic routes for the fabrication of large ensembles of functional nanosystems is to utilize self-assembly to assemble building blocks such as colloids, nanotubes, and nanowires.<sup>1–2</sup> However, if the functional nanostructures are to be assembled across many length scales within the integrated system, it is necessary to develop new tools for large-scale assembly of nanostructures and manipulation of individual components. Many approaches have been employed to control the size, shape, and position of the materials formed by the self-assembly process. These techniques include the use of patterned templates<sup>3–5</sup> and manipulation of building-blocks through electrostatic and capillary forces,<sup>6</sup> electrophoretic deposition,<sup>7</sup> and optically tunable electrophoretic assembly.<sup>8</sup> However, only in a few cases,<sup>9–10</sup> the assembly of nanostructures can be actively controlled. In this communication, we report a simple approach to actively control the formation of the self-assembled colloidal crystals in the microfluidic networks.

Colloidal particles have been used as the building blocks for the fabrication of various novel functional materials.<sup>3,5</sup> These self-assembled opaline lattices of colloidal particles, which exhibit very unique optical properties, have been used as sensors,<sup>11–13</sup> switches,<sup>14</sup> and other types of optical and electric devices.<sup>15</sup> To utilize colloidal crystals as optical components, Ozin and co-workers<sup>16–18</sup> have employed evaporation-induced self-assembly to grow colloidal crystals in the microchannels, which allowed easy integration with other planar optical components such as waveguides or fiber optics.

Another advantage of growing colloidal crystals in the microchannels is that it is possible to fabricate a large-scale integrated microfluidic system<sup>19</sup> allowing precise control of solution inside the microchannel networks. However, so far the formation of colloidal crystals in the microchannels has only been achieved through the evaporation-induced self-assembly, which is an uncontrolled process. In this process, the capillary forces can drive the colloidal solution to fill up the microchannel networks as long as the microchannels are connected. To construct a functional device, it is important to control the formation of the colloidal crystal in a designed fashion.

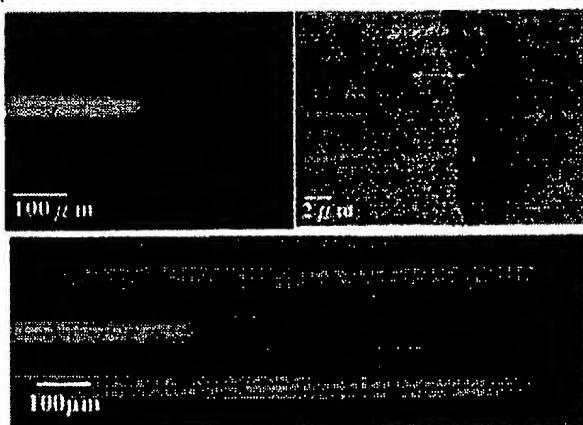
To actively control the formation of colloidal crystals inside the microchannel networks, we have employed a strategy that utilizes a combination of electrocapillary forces and evaporation-induced self-assembly.<sup>16–18</sup> Electrocapillary forces<sup>20</sup> have been demonstrated to be capable of controlling fluidic motion in three-dimensional structures. It has been suggested that the same principle can be employed to guide the microparticles or microcapsules through three-dimensional networks of channels. Our approach is to employ the electrocapillary forces to drive the colloidal solution into the predesigned position inside the microfluidic channels, and then the colloidal crystals can be obtained after solvent evaporation.

The microfluidic devices were fabricated by a replica-molding<sup>21</sup> process using poly(dimethylsiloxane) (PDMS, Sylgard 184). A



**Figure 1.** (a) ITO electrodes were fabricated under alternative microchannels. The shaded regions are ITO electrodes, and the common input reservoir is on the left. (b) Colloidal crystal formed in a single microchannel using 198-nm diameter polystyrene beads. (c) Colloidal crystals formed in three microchannels using 250-nm diameter polystyrene beads. (d) Colloidal crystals formed in two microchannels using 198- and 300-nm diameter polystyrene beads.

typical device is about  $2 \times 1 \text{ cm}^2$ , which consists of parallel microchannels ( $50 \mu\text{m}$  wide,  $8 \mu\text{m}$  high) and two common reservoirs at both ends. To control the electrocapillary forces, ITO glasses were etched into  $100\text{-}\mu\text{m}$  wide lines, which were separated at twice the distance between the microchannels so that only alternative microchannels can be influenced by the electrocapillary forces. For bonding and insulation purpose, the patterned ITO glasses were coated with  $10\text{-}\mu\text{m}$  thick PDMS, sealed against the microchannels, and cured in an oven at  $95^\circ\text{C}$ . The optical image of the microfluidic system is shown in Figure 1a, where the shaded regions are the ITO electrodes. To fabricate colloidal crystals in the microchannels, the monodispersed polystyrene particles (Bangs Laboratories, Inc.) were first mixed with  $\text{KNO}_3$  solution ( $10^{-4} \text{ M}$ , 1:1), and then the colloidal solution was injected into the reservoir. The surface tension prevented the colloidal solution from penetrating into the microchannels without the applied voltage. However, after  $150 \text{ V}$  was applied to one of the electrodes, the colloidal solution started to move into the corresponding microchannel. The electrocapillary forces could drive the solution all the way into the other end of microchannel as long as the voltage remained on. The moving speed of the colloidal solution at  $150 \text{ V}$  was estimated to be about  $25 \mu\text{m/s}$ , which depended on the thickness of the insulating PDMS layer and the quality of the microchannels. When the applied voltage was removed, the colloidal solution stopped moving forward. After solvent evaporation, the colloidal particles self-assembled into close-packed structures forming colloidal crystals in the microchannels. Figure 1b shows the optical micrograph of the colloidal crystal



**Figure 2.** (a) Two adjacent colloidal crystals formed in the same microchannel using 250- and 300-nm diameter polystyrene beads. (b) SEM image of the boundary between two adjacent colloidal crystals. (c) Three adjacent colloidal crystals formed in the same microchannel using 250-, 300-, and 198-nm diameter polystyrene beads.

formed in a single microchannel using 198-nm polystyrene beads. Both polystyrene and silica nanoparticles have been successfully used to fabricate colloidal crystals in the microchannels. This approach produced face-centered cubic (*fcc*) colloidal crystals with (111) planes oriented to the surface (Supporting Information).

Multiple channels could be addressed simultaneously or individually, depending on how the electrodes were configured. Using our approach, we can actively control the movement of the colloidal solution in each microchannel by electrocapillary forces, which can be manipulated by the applied voltage through the underlying ITO electrodes. Shown in Figure 1c are the colloidal crystals formed in three microchannels using 250-nm polystyrene nanoparticles with a common voltage supply. To further demonstrate the addressability of our technique, 150 V was applied to the first electrode allowing 198-nm polystyrene colloidal solution to fill up the first microchannel. The remaining solution in the reservoir was removed, and the second colloidal solution (300-nm polystyrene) was injected into the reservoir. At this time, the voltage on the first electrode was removed, and the second electrode was applied with 150 V. The colloidal solution occupied the second microchannel forming colloidal crystal after the solvent evaporated. Since the colloidal crystals in two different microchannels were made of different diameter of nanoparticles, they exhibited different colors as shown in Figure 1d.

In many applications, especially when the colloidal crystals are used as waveguides, composition modulation along the direction of light propagation may be needed. Our scheme allows growing several types of colloidal crystals with different optical properties inside the microchannels. The position and length of colloidal crystals can also be controlled by the applied voltage and the amount of nanoparticles in the reservoir. To construct colloidal crystals with different components in the same microchannel, the first colloidal solution was injected into reservoir, and then the voltage was applied to the corresponding electrode. When the first colloidal solution was moved to the desired position, the second colloidal solution was injected to the reservoir. By controlling the applied voltage, two adjacent colloidal crystals can be obtained at the desired position. Figure 2a shows the formation of two adjacent colloidal

crystals using this approach. Since the diameters between two different components were different, there was always a disordered region at the boundary between two colloidal crystals, which expanded a few micrometers as seen in Figure 2b. We have observed that the disordered region increased as the diameter difference between the nanoparticles increased. It should be noted that the crack formed at the interface was mainly due to the size-mismatch between two components, and the cracks seen in the other part of microchannels were formed as the result of polystyrene shrinkage during the drying process. We have successfully utilized the same method to fabricate colloidal crystals with three different colors in the same channel as shown in Figure 2c. In principle, there is no limit on the number of components that can be fabricated inside the same microchannel.

In conclusion, we have demonstrated a simple approach to actively control the self-assembly process of the colloidal nanoparticles to form colloidal crystals inside the microchannel networks using a combination of electrocapillary forces and evaporation-induced self-assembly. Using this approach, we can not only selectively fabricate the colloidal crystals in the desired channels, but we can also build colloidal crystals with different optical properties in different channels or in the same channel. This method is not limited to the fabrication of colloidal crystals. In general, it can be configured to produce other novel functional materials using the self-assembly process when it is integrated with a more sophisticated microfluidic system.

**Acknowledgment.** This research was supported in part by National Science Council, Taiwan, under Contract 92-2113-M-001-036.

**Supporting Information Available:** Figure a showing top view, and Figure b, cross-sectional SEM images of colloidal crystals formed in the microchannel using 250-nm polystyrene nanoparticles. Figure c showing reflection spectra of colloidal crystals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA048059J

# Growth of Large Colloidal Crystals with Their (100) Planes Orientated Parallel to the Surfaces of Supporting Substrates\*\*

By Yadong Yin and Younan Xia\*

Immersion against two-dimensional (2D) regular arrays of square pyramids patterned on Si(100) wafers has been exploited to fabricate colloidal crystals with their (100) planes oriented parallel to the substrates (see Figure for an SEM image). The capability and feasibility of this method have been demonstrated by crystallizing 1.0, 0.46, and 0.25  $\mu\text{m}$  polystyrene beads into 3D opaline lattices having such an orientation over areas as large as several square centimeters. Like their (111)-oriented cousins, these long-range ordered lattices of spherical colloids are useful in many areas such as photonic and optical materials. In particular, the ability to generate large colloidal crystals with adjustable spatial orientations will allow one to systematically investigate their photonic band structures in an effort to elucidate the structure-property relationships.



## 1. Introduction

Colloidal crystals are three-dimensionally periodic lattices assembled from monodispersed, spherical colloids.<sup>[1]</sup> The ability to crystallize spherical colloids into spatially periodic structures has allowed one to obtain interesting and often useful functionality not only from the constituent colloidal particles, but also from the long-range order exhibited by these periodic structures. The beautiful and attractive iridescence (opalescence) of a natural opal, for instance, can be attributed to the periodic modulation of refractive index contrast between silica colloids and the surrounding medium that are both colorless by themselves.<sup>[2]</sup> Over the past several decades, colloidal crystals have been extensively exploited as model systems to experimentally probe fundamental physical phenomena such as crystallization, melting, and many other types of phase transitions.<sup>[3]</sup> These periodic structures have also been actively explored as functional components in fabricating new types of diffractive devices such as filters and switches,<sup>[4]</sup> smart optical

sensors,<sup>[5]</sup> and photonic bandgap (PBG) structures.<sup>[6]</sup> As a matter of fact, recent studies on the unique optical properties of these materials have now evolved into a new, exciting field of research that is often referred to as photonic (bandgap) crystals.<sup>[7]</sup>

## 2. Control over Crystal Orientation

A variety of methods have been successfully demonstrated to assemble spherical colloids into crystalline lattices, with notable examples including sedimentation in the gravitational field,<sup>[8]</sup> self-organization via entropic forces or repulsive electrostatic interactions,<sup>[9]</sup> and crystallization through attractive capillary forces caused by solvent evaporation.<sup>[10]</sup> We have also developed a convenient method that utilized the hydrodynamic flow and physical confinement of a specially designed cell to crystallize spherical colloids (polystyrene or silica beads) into 3D opaline lattices with relatively large domain sizes.<sup>[11]</sup> When flat substrates were used as solid supports, all these methods could only provide face centered cubic (fcc) lattices with their (111) planes oriented parallel to these substrates. As a result of this restriction, almost all optical measurements on colloidal crystals have been limited to the [111] direction of an fcc lattice, or the L-point of their reciprocal lattice.<sup>[12]</sup>

To obtain colloidal crystals with planes other than (111)-oriented parallel to the supporting substrates, one needs to pattern the surfaces of these substrates with appropriate arrays of relief structures. These relief patterns can serve as tem-

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plates to direct and control the nucleation and growth of colloidal crystals with adjustable orientations. For example, van Blaaderen et al. have successfully grown (100)- and (110)-oriented crystals by introducing patterned substrates into a slow sedimentation process.<sup>[13]</sup> Yodh and co-workers have obtained colloidal crystals with (100) orientations by utilizing periodically patterned substrates as the supports for entropically driven self-organization.<sup>[14]</sup> The templates involved in these two studies have one major drawback: that is, the feature sizes of both templates have to be kept on the same order as the dimensions of the spherical colloids. To crystallize colloids with diameters smaller than 0.5  $\mu\text{m}$ , one needs to use advanced nanolithographic techniques (such as e-beam writing) to fabricate the templates. A new type of template recently demonstrated by Ozin's group overcomes this difficulty by using relief structures with tapered dimensions.<sup>[15]</sup> For example, Ozin and co-workers have used square pyramidal pits anisotropically etched in Si(100) wafers to fabricate small photonic crystals with their (100) planes oriented parallel to the silicon substrates. Xia and co-workers further extended the use of such a template to assemble spherical colloids into aggregates with well-defined square pyramidal shapes.<sup>[16]</sup> Here we demonstrate that the same type of template can also be adopted to generate large colloidal crystals with (100) planes oriented parallel to the solid supports by controlling the lateral dimensions of and separations between the square pyramidal pits. In this case, the feature size on the template could be many times larger than the diameters of spherical colloids to be crystallized.

### 3. Colloidal Crystals with (100) Orientation

Figure 1A shows a cross-sectional view of the flow cell that was fabricated by sandwiching a rectangular gasket ( $\approx 21 \mu\text{m}$  thick, cut from Mylar film) between two rigid substrates.<sup>[17]</sup> The bottom substrate was a piece of Si(100) wafer whose surface had been patterned with a regular 2D array of square pyramidal pits through anisotropic etching in an aqueous solution containing KOH and 2-propanol.<sup>[18]</sup> The protection mask was, in turn, fabricated in a thin film ( $\approx 300 \text{ nm}$  thick) of gold sputtered on the Si(100) substrate. Both microcontact printing with alkanethiols and conventional photolithography with resists could be used to define the pattern.<sup>[19]</sup> The top substrate was a piece of flat glass slide. A hole of  $\approx 3 \text{ mm}$  in diameter was generated in this glass slide by drilling with a diamond-coated tool. A glass tube of  $\approx 6 \text{ mm}$  in diameter was attached to this hole using epoxy adhesive. The cell could be held together using several binder clips. After an aqueous dispersion of polystyrene beads ( $\approx 5 \text{ wt.}\%$ ) was injected into the glass tube through a syringe, the opening of this inlet was sealed with Parafilm to prevent solvent evaporation. This cell was placed in an empty beaker immersed in the water bath of an ultrasonic cleaner (Branson 2210) to allow the polymer beads to crystallize into a long-range ordered lattice. Depending on the sizes of channels between the Mylar film and solid sub-

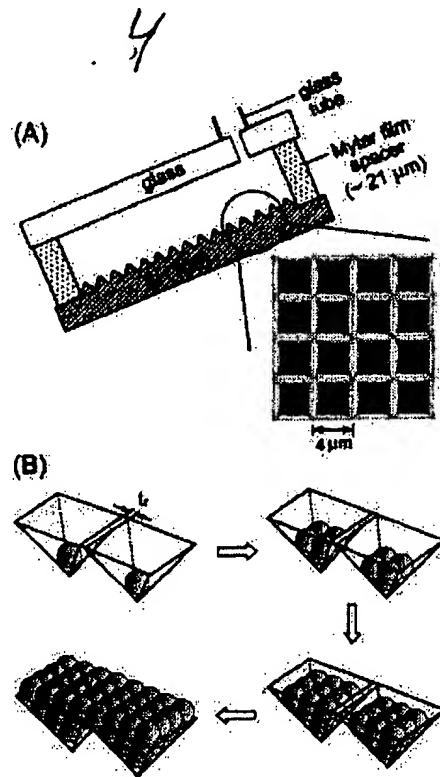


Fig. 1. A) A schematic illustration of the flow cell that was used to crystallize monodispersed, spherical colloids into 3D opaline lattices with their (100) planes oriented parallel to the surfaces of substrates. The key component is a regular 2D array of square pyramidal pits (inset) that have been patterned in the surface of the bottom substrate – Si(100) wafer. B) Step-by-step formation of a (100)-oriented 3D opaline lattice by templating against the 2D array of square pyramidal pits.

strates and the diameters of polymer beads, one could obtain opaline lattices over  $\approx 1 \text{ cm}^2$  within a few days. As shown in Figure 1B, the polymer beads were directed by the square pyramidal pits in Si(100) surface to grow into an opaline lattice with its (100) planes oriented parallel to the surface of the bottom or top substrate. In this templating process, the atomic scale symmetry of the underlying Si(100) single crystal was faithfully transferred into the mesoscale opaline lattice.

Figure 2 shows the scanning electron microscopy (SEM) images of a sample fabricated by crystallizing 1.0  $\mu\text{m}$  polystyrene beads in a cell of  $\approx 21 \mu\text{m}$  thick. Figure 2A shows the top view of a portion of this opaline lattice, clearly indicating the square symmetry of (100) planes parallel to the surfaces of both top and bottom substrates. Since water had completely evaporated from the cell before the top substrate was removed, some polystyrene beads stuck to the top substrate and resulted in a rough morphology for the surface shown in Figure 2A. Figures 2B and 2C show oblique SEM images of two portions of the same colloidal crystal that happened to stay with the bottom and top substrates, respectively, when the cell was disassembled. The crystalline seeds that grew inside the square pyramidal pits are clearly seen in Figure 2C, although their structures have been partially destroyed. These SEM images suggested that the 3D lattices generated using the present procedure exhibit long-range ordering along both directions parallel and perpendicular to the surface of the bottom

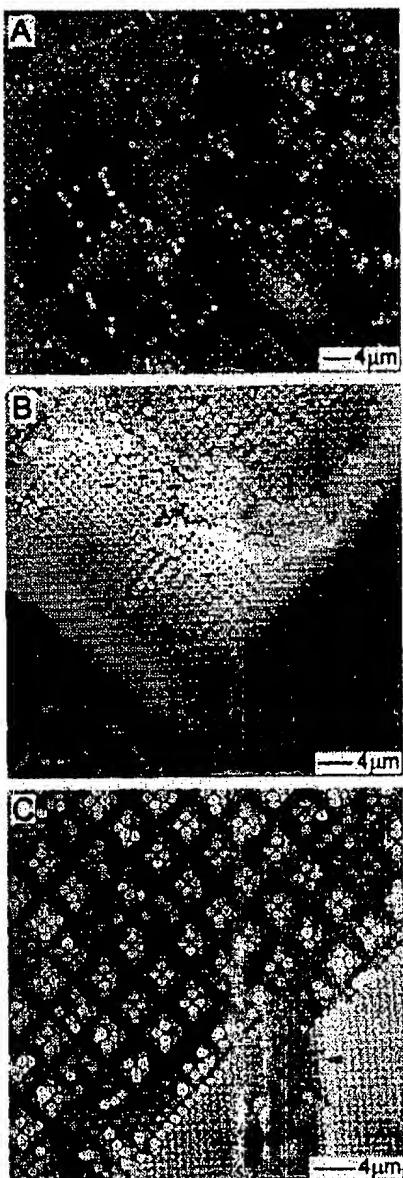


Fig. 2. SEM images of a (100)-oriented opaline lattice of 1.0  $\mu\text{m}$  polystyrene beads generated by templating against an array of square pyramidal pits. A) A top view of this opaline lattice after the top glass substrate has been removed. When the top glass substrate was separated from the cell, some portions of this opaline lattice stuck to the top substrate, and some portions were left behind on the bottom substrate. B) The oblique view of a portion of this sample remaining on the 2D array of square pyramidal pits. C) The oblique view of another portion of this sample sticking to the top substrate. This image shows both cross-section and bottom surface of this 3D opaline lattice.

substrate. As we demonstrated previously, such a 3D periodic structure could also be assigned as a fcc lattice with the (100) planes parallel to the surface of either top or bottom substrate.<sup>[20]</sup>

Figure 3 shows SEM images of two additional samples that were fabricated by crystallizing 0.48  $\mu\text{m}$  and 0.25  $\mu\text{m}$  polystyrene beads in cells of  $\approx$ 20  $\mu\text{m}$  thick. Again, both SEM images clearly indicate that the (100) planes of these two colloidal

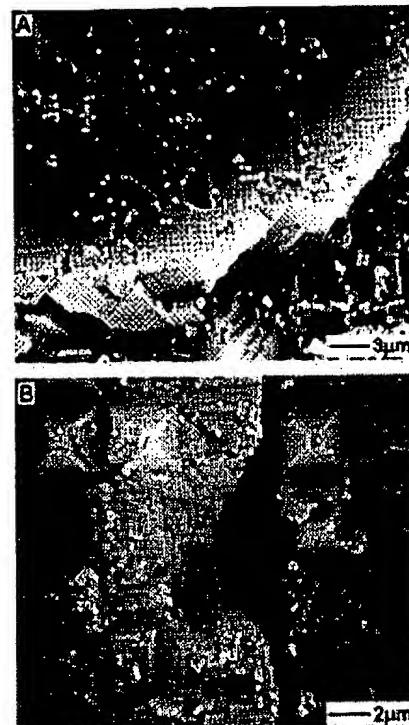


Fig. 3. Top-view SEM images of (100)-oriented opaline lattices that were crystallized from A) 0.48  $\mu\text{m}$  and B) 0.25  $\mu\text{m}$  polystyrene beads. Both images clearly indicate that the (100) planes (with a square symmetry) of these colloidal crystals have been oriented parallel to the substrates.

crystals have been oriented parallel to the top or bottom substrate through templating. We believe that the present approach could be extended to spherical colloids with even smaller diameters as long as the width of ridges ( $t_r$ ) that separate square pyramidal pits could be reduced to smaller scales. The current dimension is  $\approx$ 250 nm (as shown in the inset of Fig. 1A), and was mainly limited by the silicon etching procedure.

#### 4. Conclusions

In summary, we have demonstrated that it is possible to fabricate (100)-oriented colloidal crystals by employing regular 2D arrays of square pyramidal pits as the templates to control the spatial orientation. There are at least two advantages associated with this method: First, there is no need to use e-beam writing (not even the clean room facilities once the elastomeric stamps for microcontact printing has been fabricated) to prepare the templates to be used with spherical colloids smaller than 500 nm. Second, the silicon templates should be robust enough to be reused for many times, if necessary. As demonstrated previously, replica molding can be readily used to generate numerous copies of the template in rigid polymers such as epoxy or polyurethane.<sup>[21]</sup> Note that both replica molding and colloidal crystallization processes could be carried out in an ordinary chemistry laboratory, without use of

clean room facilities. The simplicity of these approaches should allow more research groups to generate 3D opaline arrays of spherical colloids in their own laboratories, and then explore their uses in various applications. This ability to control the orientation of an opaline lattice provides another useful way to change the photonic and structural properties of these colloidal crystals.

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